(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 March 2002 (14.03.2002)

PCT

(10) International Publication Number
WO 02/19846 A2

(51) International Patent Classification[7]: A23L 3/3508, 3/3526, 3/358

(21) International Application Number: PCT/US01/41954

(22) International Filing Date: 30 August 2001 (30.08.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/655,131 5 September 2000 (05.09.2000) US

(71) Applicant: MIONIX CORPORATION [US/US]; Suite 130, 1376 Lead Hill Boulevard, Roseville, CA 95661 (US).

(72) Inventors: KEMP, Maurice, Clarence; 4401 Woodthrush Drive, El Dorado Hills, CA 95762 (US). LALUM, Robert, Blaine; 6949 Greenback Lane #B, Citrus Heights, CA 95621 (US). LEWIS, David, E.; 816 Third Avenue, Eau Claire, WI 54703 (US). CARPENTER, Robert, H.; 1303 Pecan Street, Bastrop, TX 78602 (US).

(74) Agent: CHWANG, T., Ling; Jackson Walker, L.L.P., Suite 600, 2435 N. Central Expressway, Richardson, TX 75080 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: HIGHLY ACIDIC METALATED ORGANIC ACID

(57) Abstract: A highly acidic metalated organic acid composition and its preparation. The acidic composition can be prepared by mixing a monovalent or polyvalent cation and an organic acid in the presence of a strong oxyacid, wherein the resultant acidic composition is less corrosive to a ferrous metal than a solution of a mineral acid having the same acidic pH value as that of the acidic composition, and where in the acid composition is more biocidal than a mixture of the organic acid and metal salt of the organic acid which the mixture has the same acid normality value as that of the acidic composition. The acidic composition can be prepared by mixing at least one regenerating acid, at least one metal base, and at least one organic acid, wherein the amount of the regenerating acid is in excess of the equivalent amount of the metal base.

HIGHLY ACIDIC METALATED ORGANIC ACID

BACKGROUND

This invention relates to a highly acidic metalated organic acid and its preparation.

5   Organic acids and alcohols have been used throughout recorded history as ingredients to decontaminate and preserve food and other biological materials. The pickling process using acetic acid is the food preservation method most familiar to the
10   public. Large numbers of other organic acids have also been used in food processing. The addition of an organic acid to foodstuffs is called acidulation. Acidulated foods are defined in the Code of Federal Regulations (21 CFR) as any consumable food product
15   with a pH of less than 4.6 and produced to comply with current Good Manufacturing Practices ("cGMP") for food and food additives. These products have cost and taste advantages over heat-treated foods. Acidulated foods give a better taste of "freshness"
20   than those that have been heat treated.

Another common method of food preservation and preparation utilizes heat followed by drying, packaging or canning to prevent contamination. Heat-treated foods retain qualities of freshly prepared
25   food but, nevertheless, give the canned food taste. As energy cost continues to rise, the percentage of production cost due to energy may make some food preparation and/or production costs prohibitive. Additionally, new packaging and other regulatory
30   costs will certainly drive up the cost of food..

Newer methods of food preservation include the addition of non-pathogenic bacteria to prevent spoilage and irradiation with ionizing radiation for preservation. Each of these methods has cost,
5   quality and food safety issues associated with implementation. Acidulation of food with mineral and/or organic acids remains the least costly and most effective method of food preservation.

In the late 80's and early 90's, researchers in
10 Japan developed strong ionized water ("SIW") as disinfectants. The SIW was established as water with pH 2.7 or less, having an oxidation-reduction potential of 1,000 mv or more, and chlorine concentration of 0.8 ppm or more. The SIW is
15 prepared by electrolysis of water.

Electrolysis of tap water has also been used to produce "strong acid water" and "strong alkali water" both of which were claimed to have antiseptic properties.

20   U.S. Patent Number 5,830,838 to Wurzburger, et al. describes a solution for cleaning metal surfaces. The solution is prepared by mixing calcium hydroxide and potassium hydroxide with equivalent sulfuric acid in water then passing the solution through a 10
25 micron filter. The resulting concentrate can be diluted depending on the degree of surface oxidation of the metal to be treated.

U.S. Patent Number 5,895,782 to Overton, et al. describes a solution for cleaning metal surfaces
30 particularly non-ferrous alloys such as copper, brass and high strength aluminum alloys. The solution is prepared by mixing $Ca(OH)_2$ and KOH with equivalent sulfuric acid in water then passing the solution

through a 10 micron filter. The resulting
concentrate can be used full strength or diluted
depending on the degree of surface oxidation of the
metal to be treated.

5   International Publication WO 94/09798 describes
a pharmaceutical composition for treatment of
disease, injury and other disorders. The
pharmaceutical composition comprises a complex of a
calcium-containing component and a sulfate-containing

10   component in a pharmaceutically acceptable carrier.
The reference teaches the isolation from natural
materials, such as peat, the inorganic compositions.
The inorganic preparations comprise an alkaline,
aqueous or organic, or mixture thereof, extract of

15   peat. Peat is extracted with aqueous solutions,
organic solutions or water-miscible organic solvents
at temperature from below room temperature up to the
boiling point of the solvents. The preferred
extracting solvents are those having a pH of at least

20   9. Biologically active constituents of fractionated
peat preparations were identified as $CaSO_4 \cdot 2H_2O$
(gypsum), $CaSO_4 \cdot K_2SO_4 \cdot H_2O$ (syngenite, also referred to
as the double salt of gypsum) and $K_3Na(SO_4)_2$
(apthitalite) by X-ray powder diffraction analysis.

25   The reference also describes the synthesis of
syngenite.

        Chemists describe and measure the ability of a
substance to donate protons [H^+] to a chemical
reaction as the pKa of that substance where

30

$$HA + H_2O \rightarrow H_3O^+ + A^-$$

-4-
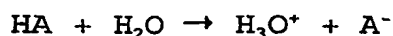
Although a hydronium ion is usually represented by H_3O^+, its true formula is not certain, and best represented as $H^+ \cdot (H_2O)_n$. The aggregate could be $H_5O_2^+$, $H_7O_3^+$, $H_9O_4^+$, or even larger.

5   Hydrated hydronium ion has the ability to donate protons $[H^+]$. The donation of a proton is usually an intermediate step in any acid hydrolysis reaction. Acids are usually the chemical reagents used to donate protons in an aqueous solution.

10   A strong acid is used to neutralize and remove the lime, or quicklime, from bricks and mortar. A strong acid, such as hydrochloric acid, also known as muriatic acid, is also used to clean hard water spots on shower stalls, windows, glass, toilets, urinals,

15   mirrors and other surfaces. Hydrochloric acid is used to de-scale water towers and heat exchangers and to adjust the pH of waste water effluent. A full strength mineral acid, such as hydrochloric acid, is extremely corrosive to many substances, including

20   metals. In addition, hydrochloric acid at a low pH of 0.5 or so can burn a sensitive human skin in a very short period of time. The acid is also very harmful in that it emits fumes irritating to the mucous membrane. If left near other chemicals, like

25   bleach, hydrochloric acid will interact with them, even through a typical plastic bottle.

It is thus desirable to be able to have a source of "acidity," or H_3O^+, without these unwanted disadvantages and be able to reduce environmental and

30   safety hazards associated with acid hydrolysis. Preferably, this source of "acidity" should be able to prevent re-contamination following decontamination, not induce bacterial resistance, not

alter the taste, color or smell of treated
foodstuffs, not create any odor, effective in water
in a wide range of temperatures, relatively free of
danger when overdosed, can be neutralized after use,

5   not carcinogenic or mutagenic, non-toxic, almost
harmless in water and the environment,environmentally
friendly, and can. be stored for a long period of time
without decomposition or turning into hazardous
compound.

10   The control of microbial growth is necessary in
many practical situations, and significant advances
in agriculture, medicine and food science have been
made through study of this area of microbiology.
"Control of growth" means to prevent growth of

15   microorganisms. This control is effected in one of
two basic ways: (1) By killing microorganisms; or
(2) by inhibiting the growth of microorganisms.
Control of growth usually involves the use of
physical or chemical agents which either kill or

20   prevent the growth of microorganisms. Agents which
kill cells are called "cidal" agents; agents which
inhibit the growth of cells, but without killing
them, are referred to as "static" agents. Thus the
term "bactericidal" refers to killing bacteria and

25   "bacteriostatic" refers to inhibiting the growth of
bacterial cells. A "bactericide" kills bacteria, a
"fungicide" kills fungi. "Sterilization" is the
complete destruction or elimination of all viable
organisms in or on an object being sterilized. The

30   object is either sterile or not, there are no degrees
of sterilization. Sterilization procedures involve
the use of heat, radiation or chemicals, or physical
removal of microorganisms.

Microorganisms tend to colonize and replicate on
different surfaces resulting in adherent heterogenous
microbial accumulations termed "biofilms." Biofilms
may form on surfaces of food substances, feed
5   substances, processing equipment and
instrumentations. The microorganisms in the biofilms
may include bacteria, fungi, viruses, and protozoans.
Since food safety is a national priority, any product
that can help by solving a multitude of problems
10 associated with food production is desirable.
Removal and control of biofilms which harbor
dangerous microbial contamination is a sanitation
goal that needs to be achieved. It is also desirable
to be able to safely decontaminate water and
15 nutriment by lowering pH to levels where contaminants
would react and organisms cannot live.

Current sanitizing, disinfectant and pesticide
products on the market for these uses contain
residues of chlorine, ammonia, organic iodine, metal
20 salts and other deleterious residues. It is desirable
to have a way that would preclude these residues by
promoting acid hydrolysis without the presence of
deleterious chemicals. Additionally, this method
should generate few hazardous volatile gases.
25 Importantly, it is highly desirable to have a
composition that can control the growth of, and kill,
microorganisms and, at the same time, destroy the
products, generated by, or associated with, the
microorganisms.

SUMMARY

The present invention involves a highly acidic
metalated organic acid composition and its
preparation. One embodiment of the present invention
5   pertains to an acidic composition having an acidic pH
value and an acid normality value. The acidic
composition is prepared by mixing a monovalent or
polyvalent cation and an organic acid in the presence
of a strong oxyacid, wherein the resultant acidic
10   composition is less corrosive to a ferrous metal than
a solution of a mineral acid having the same acidic
pH value as that of the acidic composition, and
wherein the acid composition is more biocidal than a
mixture of the organic acid and a metal salt of the
15   organic acid which mixture has the same acid
normality value as that of the acidic composition.
The acidic composition can be prepared by mixing at
least one regenerating acid, at least one metal base,
and at least one organic acid, wherein the amount of
20   the regenerating acid is in excess of the equivalent
amount of the metal base. One aspect of the present
invention pertains to method of preparing the highly
acidic metalated organic acid.

DETAILED DESCRIPTION

25

One aspect of the present invention pertains to
a composition of a highly acidic metalated organic
acid ("HAMO"). The composition may have a suspension
of very fine particles, and it has a monovalent or a

polyvalent cation, an organic acid, and an anion of a
regenerating acid, such as the anion of a strong
oxyacid. The term "highly acid" means the pH is in
the acidic region, below at least about 4. HAMO of
5   the present invention is less corrosive to a ferrous
metal than a solution of a mineral acid having the
same acidic pH value as that of the acidic
composition. HAMO is also more biocidal than a
mixture of the organic acid and a metal salt of the
10   organic acid which mixture having the same acid
normality value as that of the acidic composition.
        Broadly, one way HAMO can be prepared is by
mixing the following ingredients: (1) at least one
regenerating acid; (2) at least one metal base; and
15   (3) at least one organic acid, wherein the equivalent
amount of the regenerating acid is in excess of the
equivalent amount of the metal base. The equivalent
amount of the metal base should be about equal to
that of the organic acid. Instead of using a metal
20   base and an organic acid, a metal salt of the organic
acid can be used in place of the metal base and the
organic acid. The insoluble solid is removed by any
conventional method, such as sedimentation,
filtration, or centrifugation.
25   Generally, HAMO can be prepared by blending or
mixing the necessary ingredients in at least the
following manners:

        1.   Regenerating acid + (metal base + organic
              acid);
30   2.   Regenerating acid + (metal base + salt of
              organic acid);

3.   (Regenerating acid + salt of organic acid)
      + base; and

4.   Regenerating acid + salt of organic acid.

5   The parenthesis in the above scheme denotes
"pre-mixing" the two ingredients recited in the
parenthesis. Normally, the regenerating acid is
added last to generate the HAMO. Although each of
the reagents is listed as a single reagent,
optionally, more than one single reagent, such as

10   more than one regenerating acid or organic acid, can
be used in the current invention. The number of
equivalents of the regenerating acid must be larger
than the number of equivalents of the metal base, or
those of the metal salt of the organic acid. When

15   the organic acid is an amino acid, which, by
definition contains at least one amino group, then
the number of equivalents of the regenerating acid
must be larger than the total number of equivalents
of the metal base, or metal salt of the organic acid,

20   and the "base" amino group of the amino acid. Thus,
the resultant highly acidic metalated organic acid is
different from, and not, a buffer.
       As used herein, a regenerating acid is an acid
that will "re-generate" the organic acid from its

25   salt. Examples of a regenerating acid include a
strong binary acid, a strong oxyacid, and others. A
binary acid is an acid in which protons are directly
bound to a central atom, that is (central atom)-H.
Examples of a binary acid include HF, HCl, HBr, HI,

30   H_2S and HN_3. An oxyacid is an acid in which the
acidic protons are bound to oxygen, which in turn is

bound to a central atom, that is (central atom)-O-H. Examples of oxyacid include acids having Cl, Br, Cr, As, Ge, Te, P, B, As, I, S, Se, Sn, Te, N, Mo, W, or Mn as the central atom. Some examples include H_2SO_4,

5   HNO_3, H_2SeO_4, $HClO_4$, H_3PO_4, and $HMnO_4$. Some of the acids (e.g. $HMnO_4$) cannot actually be isolated as such, but occur only in the form of their dilute solutions, anions, and salts. A "strong oxyacid" is an oxyacid which at a concentration of 1 molar in water gives a

10 concentration of H_3O^+ greater than about 0.8 molar.

    The regenerating acid can also be an acidic solution of sparingly-soluble Group IIA complexes ("AGIIS"). AGIIS can be prepared by mixing or blending materials given in one of the following

15 scheme with good reproducibility:

        (1) H_2SO_4 and $Ca(OH)_2$;
        (2) H_2SO_4, $Ca(OH)_2$, and $CaCO_3$;
        (3) H_2SO_4, $Ca(OH)_2$, $CaCO_3$, and CO_2 (gas);
        (4) H_2SO_4 and $CaCO_3$;

20   (5) H_2SO_4, $CaCO_3$, and $Ca(OH)_2$;
        (6) H_2SO_4, $CaCO_3$, and CO_2 (gas);
        (7) H_2SO_4 and $CaSO_4$;
        (8) H_2SO_4, $Ca(OH)_2$, and $CaSO_4$;
        (9) H_2SO_4, $CaSO_4$, and $CaCO_3$;

25   (10) H_2SO_4, $CaSO_4$, $CaCO_3$, and $Ca(OH)_2$;
        (11) H_2SO_4, $CaSO_4$, $CaCO_3$, and CO_2 (gas); and
        (12) H_2SO_4, $CaSO_4$, $CaCO_3$, CO_2 (gas), and $Ca(OH)_2$.

    Thus, preferably, AGIIS is prepared by mixing

30 calcium hydroxide with concentrated sulfuric acid, with or without an optional Group IIA salt of a dibasic acid (such as calcium sulfate) added to the sulfuric acid. The optional calcium sulfate can be

added to the concentrated sulfuric acid prior to the
introduction of calcium hydroxide into the blending
mixture.   The addition of calcium sulfate to the
concentrated sulfuric acid appears to reduce the
5   amount of calcium hydroxide needed for the
preparation of AGIIS.   Other optional reagents
include calcium carbonate and gaseous carbon dioxide
being bubbled into the mixture.   Regardless of the
use of any optional reagents, it was found that the
10   use of calcium hydroxide is desirable.

One preferred method of preparing AGIIS can be
described briefly as: Concentrated sulfuric acid is
added to chilled water (8°-12°C)in the mixing vessel,
then, with stirring, calcium sulfate is added to the
15   acid in chilled water to give a mixture. Temperature
control is paramount to this process. To this
stirred mixture is then added a slurry of calcium
hydroxide in water. The solid formed from the
mixture is then removed. This method involves the
20   use of sulfuric acid, calcium sulfate, and calcium
hydroxide, and it has several unexpected advantages.
Firstly, this mixing is not violent and is not
exceedingly exothermic. Besides being easy to
control and easy to reproduce, this mixing uses
25   ingredients each of which has been reviewed by the
U.S. Food and Drug Administration ("U.S. FDA") and
determined to be "generally recognized as safe"
("GRAS"). As such, each of these ingredients can be
added directly to food, subject, of course, to
30   certain limitations. Under proper concentration,
each of these ingredients can be used as processing
aids and in food contact applications. Their use is

limited only by product suitability and Good
Manufacturing Practices ("GMP").

    The sulfuric acid used in the preparation of
AGIIS or for this invention is usually 95-98% FCC

5   Grade (about 35-37 N). Concentration of sulfuric
acid used to generate AGIIS can range from about 0.05
M to about 18 M (about 0.1 N to about 36 N),
preferably from about 1 M to about 5 M. It is
application specific. The term "M" used denotes

10   molar or moles per liter.

    In the preparation of AGIIS, normally, a slurry
of finely ground calcium hydroxide suspended in water
(about 50% of W/V) is the preferred way of
introducing the calcium hydroxide, in increments,

15   into a stirred solution of sulfuric acid, with or
without the presence of calcium sulfate. Ordinarily,
the mixing is carried out below 40°C, preferably
below room temperature, and more preferably below
10°C. The time to add calcium hydroxide can range

20   from about 1 hour to about 4 hours. The agitation
speed can vary from about 600 to about 700 rpm, or
higher. After mixing, the mixture is filtered
through a 5 micron filter. The filtrate is then
allowed to sit overnight and the fine sediment is

25   removed by decantation.

    The calcium hydroxide used for AGIIS or for this
invention is usually FCC Grade of about 98% purity.
For every mole of concentrated acid, such as sulfuric
acid, the amount, in moles, of calcium hydroxide used

30   is application specific and ranges from about 0.1 to
about 1.

    The calcium carbonate is normally FCC Grade
having a purity of about 98%. When used with calcium

hydroxide as described above for the preparation of
AGIIS, for every mole of a concentrated acid, such as
sulfuric acid, the amount, in moles, of calcium
carbonate ranges from about 0.001 to about 0.2,
5   depending on the amount of calcium hydroxide used.

The optional carbon dioxide in the preparation
of AGIIS is usually bubbled into the slurry
containing calcium hydroxide at a speed of from about
1 to about 3 pounds pressure. The carbon dioxide is
10   bubbled into the slurry for a period of from about 1
to about 3 hours. The slurry is then added to the
mixing vessel containing the concentrated sulfuric
acid.

Another optional ingredient in the preparation
15   of AGIIS is calcium sulfate, a Group IIA salt of a
dibasic acid. Normally, dihydrated calcium sulfate
is used. As used in this application, the phrase
"calcium sulfate," or the formula "$CaSO_4$," means
either anhydrous or hydrated calcium sulfate. The
20   purity of calcium sulfate (dihydrate) used is usually
95-98% FCC Grade. The amount of calcium sulfate, in
moles per liter of concentrated sulfuric acid ranges
from about 0.005 to about 0.15, preferably from about
0.007 to about 0.07, and more preferably from about
25   0.007 to about 0.04. It is application specific.

An organic acid is an acidic compounds
containing carbon. It includes carboxylic acid,
amino acid, acidic vitamin, sulfonic acid, phosphonic
acid, and others. A carboxylic acid is an organic
30   compound containing an -COOH group, i.e., a carbonyl
attached to a hydroxyl group. A carboxylic acid can
be a mono-carboxylic acid, a di-carboxylic acid, or a
tri-carboxylic acid. A mono-carboxylic acid can be

represented by a general formula of R^1-COOH, wherein R^1 can be: H; C_1-C_4 saturated alkyl; C_2-C_5 unsaturated alkyl with 2 or less double bonds; or C_2-C_5 unsaturated alkyl with 2 or less triple bonds;

5   $CH_3CH(OH)$; $HOCH_2(CHOH)_4$; or $R_2CH(NH_2)$, wherein R_2 is H,C_1-C_4 saturated alkyl, $C_6H_5CH_2$, p-HO-$C_6H_4CH_2$, $H_2N(CH_2)_4$, $HOCH_2$, or CH_3CHOH. A di-carboxylic acid can be represented by a general formula of HOOC-R^3-COOH, wherein R^3 can be: $(CH_2)_m$, in which m can be 1-3;

10   (CH=CH); $CH_2CH(OH)$ $H(OH)C$-$CH(OH)$; or $(CH_2)_pCH(NH_2)$, in which p is 2 or 3. A tri-carboxylic acid can be represented by a general formula of $HOOCR^4(COOH)COOH$, wherein R^4 can be: $CH_2C(OH)CH_2$; or CH_2CHCH_2. Although some amino acids have been included in the general

15   category of mono-carboxylic acid, it is known in the art that amino acids include: alanine; arginine; aspartic acid (asparagine); cysteine (cystine); glutamic acid (glutamine); glycine; histidine; hydroxylysine; hydroxyproline; isoleucine; leucine;

20   lycine; mehtionine; phenylalanine; proline; serine; threonine; tryptophan; tyrosine; valine; aminoadipic acid; diaminobutyric; ornithine; pipecolic acid; sarcosine; and thiiodothyronine (thyroxine).

The metal base can be in the form of an OH^-,

25   CO_3^-, HCO_3^-, or O^- salt. The metal can be a monovalent metal, a polyvalent metal, all transition and rare earth elements, Sn, Pb, or Bi. Examples of monovalent metals include elements in Group IA. The polyvalent metals can be a divalent metal or a

30   trivalent metal. Examples of divalent metals include elements in Group IIA, except Be; and examples of trivalent metals include elements in Group IIIA, except B. Preferably the metal is Mn, Mg, Ca,

Fe(II), Cu(II), Zn(II), Ce, Ni, Pd, Cr, Ti, Zr, Co, Al, Sn, Pb, Bi, V(III), Cd, Hg, Pt, Hf, and other first-row lanthanides, except Pm. More preferably, the metal is Mg, Ca, Fe(II), Cu(II), Zn, Cr, or Co.

5 Salts of an organic acid as used in this application include the salts of the metals, discussed above, salts of the organic acids, also discussed above, and others.

  The term "biocidal" means destruction of a

10 biological contaminant. A "biological contaminant" is defined as a biological organism, or the product of biological organism, such as toxin, or both, all of which contaminate the environment and useful products. This biological contaminant results in

15 making the environment or product hazardous.

  Biological contaminants, such as bacteria, fungi, mold, mildew, spores, and viruses have potentially reactive substances in their cell wall/membranes; however, they hide in cells (viruses

20 and some bacteria) and/or secrete biofilms (most bacteria, fungi, mold and mildew) to protect them from the environment.

  Bacteria form or elaborate intracellular or extracellular toxins. Toxin is a noxious or

25 poisonous substances that: (1) are an integral part of the bacteria; (2) are an extracellular product (exotoxin) of the bacteria; or (3) represent a combination or the two situations, formed or elaborated during the metabolism and growth of

30 bacteria. Toxins are, in general, relatively complex antigenic molecules and the chemical compositions are usually not known. The harmful effects of bacteria come not only from the bacteria themselves, but also

from the toxins produced by bacteria. Toxins
produced by bacteria are just as, if not more,
hazardous to the product than the bacteria
themselves. Ordinary disinfectants, such as

5   quaternary ammonium compounds, will kill bacteria but
may have no effect on bacterial toxins and
endotoxins. In fact, many disinfectants actually
contribute to the endotoxins problems by causing
their release from the bacteria. The bacterial

10   toxins and endotoxins can cause serious adverse
effects in human and animals. Endotoxins are a major
cause of contamination in food products, in the
production of pharmaceuticals, medical devices, and
other medical products.

15   The outer covering, i.e. epidermis, of animals
and cuticle of plants resist the growth and/or entry
of the above microorganisms into the interior of the
complex organism. One of the microbial growth
prevention methods used by plants and animals is the

20   maintenance of a surface pH or secretion of a coating
that is not conducive to the attachment and
propagation of micro-organisms. After a plant
product is harvested or an animal product processed,
these products loose the ability to resist the

25   infestation of micro-organisms.

    The composition of the present invention was
found to be a "preservative." The composition is
minimally corrosive; however, it can create an
environment where destructive micro-organisms cannot

30   live and propagate, thus prolonging the shelf-life of
the product. As is known in the art, formic acid is
not as corrosive to a ferrous metal as is a mineral
acid, such as hydrochloric acid. Yet, formic acid

solution is more corrosive to a galvanized roofing
nail than is a solution of HAMO. In one experiment,
after 48 hours of air-drying, a galvanized roofing
nail, which had been dipped for 20 minutes at room
5   temperature in a solution of formic acid with a pH of
1.5, showed obvious, visible corrosion. Yet, under
similar conditions, no such obvious, visible
corrosion was observed for a galvanized roofing nail
having been dipped in a solution of HAMO (prepared
10   from lactic acid, calcium hydroxide and regenerated
with phosphoric acid) at a pH of 1.44.

The utility of the method of preservation
demonstrated herein is that additional chemicals do
not have to be added to the food or other substance
15   to be preserved because the inherent low pH of the
mixture is preservative. Since preservative
chemicals do not have to be added to the food
substance, taste is improved and residues are
avoided. Organoleptic testing of a number of freshly
20   preserved and previously preserved food stuffs have
revealed the addition of composition improves taste
and eliminates preservative flavors. The term
"organoleptic" means making an impression based upon
senses of an organ or the whole organism.
25   The composition of the present invention was
found to be biocidal. The composition was found to
be biocidal to E.coli, and other bacteria.

The following examples are provided to further
illustrate this invention and the manner in which it
30   may be carried out. It will be understood, however,
that the specific details given in the examples have
been chosen for purposes of illustration only and not
be construed as limiting the invention. Unless

otherwise defined, the amount of each ingredient or
component of the present invention is based on the
weight percent of the final composition.

Example 1

5 Preparation of 1.2-1.5 N AGIIS (H_2SO_4/Ca(OH)$_2$)

An amount of 1055 ml (19.2 moles, after purity
adjustment and taking into account the amount of acid
neutralized by base) of concentrated sulfuric acid
(FCC Grade, 95-98% purity) was slowly added with
10 stirring, to 16.868 L of RO/DI water in each of
mixing flasks a, b, c, e, and f. The amount of water
had been adjusted to allow for the volume of acid and
the calcium hydroxide slurry. The mixture in each
flask was mixed thoroughly. Each of the mixing
15 flasks was chilled in an ice bath and the temperature
of the mixture in the reaction flask was about 8-
12°C. The mixture was continuously stirred at a rate
of about 700 rpm.

Separately, a slurry was made by adding RO/DI
20 water to 4·kg of calcium hydroxide (FCC Grace, 98%
purity) making a final volume of 8 L. The mole ratio
of calcium hydroxide to concentrated sulfuric acid
was from about 0.45 to about 1. The slurry was a 50%
(W/V) mixture of calcium hydroxide in water. The
25 slurry was mixed well with a high-shear-force mixer
until the slurry appeared uniform. The slurry was
then chilled to about 8-12°C in an ice bath and
continuous stirred at about 700 rpm.

To each of the mixing flasks was added 150 ml of
30 the calcium hydroxide slurry every 20 minutes until
1.276 L (i.e. 638 g dry weight, 8.61 moles, of

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calcium hydroxide) of the slurry had been added to each reaction vessel. The addition was again accompanied by thorough mixing at about 700 rpm.

5 After the completion of the addition of the calcium hydroxide to the mixture in each mixing vessel, the mixture was filtered through a 5-micron filter.

The filtrate was allowed to sit for 12 hours, the clear solution was decanted to discard any
10 precipitate formed. The resulting product was AGIIS having an acid normality of 1.2-1.5. Analysis showed: Ca, 715 ppm (600 ppm - 800 ppm); SO_4, 45,700 ppm (40,000 ppm - 55,000 ppm).

Example 2
15 Preparation of 2 N AGIIS (H_2SO_4/Ca(OH)$_2$/CaSO$_4$)

For the preparation of 1 L of 2 N AGIIS, an amount of 79.54 ml (1.44 moles, after purity adjustment and taking into account the amount of acid to be neutralized by base) of concentrated sulfuric
20 acid (FCC Grade, 95-98% purity) was slowly added, with stirring, to 853.93 ml of RO/DI water in a 2 L mixing flask. Five grams of calcium sulfate (FCC Grade, 95% purity) were then added slowly and with stirring to the mixing flask. The mixture was mixed
25 thoroughly. At this point, the mixture would usually exhibit an acid normality of 2.88. The mixing flask was chilled in an ice bath and the temperature of the mixture in the reaction flask was about 8-12°C. The mixture was continuously stirred
30 at a rate of about 700 rpm.

Separately, a slurry was made by adding 49.89 ml of RO/DI water to 33.26 g (0.44 mole, after purity adjustment) of calcium hydroxide (FCC Grace, 98% purity) making a final volume of 66.53 ml. The mole

5 ratio of calcium hydroxide to concentrated sulfuric acid was from about 0.44 to about 1. The slurry was mixed well with a high-shear-force mixer until the slurry appeared uniform. The slurry was then chilled to about 8-12°C in an ice bath and continuous stirred

10 at about 700 rpm.

The slurry was then slowly added over a period of 2-3 hours to the mixture, still chilled in an ice bath and being stirred at about 700 rpm.

After the completion of the addition of slurry

15 to the mixture, the product was filtered through a 5-micron filter. It was normal to observe a 20% loss in volume of the mixture due to the retention of the solution by the salt and removal of the salt.

The filtrate was allow to sit for 12 hours, the

20 clear solution was decanted to discard any precipitate formed. The resulting product was AGIIS having an acid normality of 2.

Example 3
Preparation of 12 N AGIIS (H_2SO_4/Ca(OH)$_2$/CaSO$_4$)

25 For the preparation of 1 L of 12 N AGIIS, an amount of 434.17 ml (7.86 moles, after purity adjustment and taking into account amount of acid neutralized by base) of concentrated sulfuric acid (FCC Grade, 95-98% purity) was slowly added, with

30 stirring, to 284.60 ml of RO/DI water in a 2 L mixing

flask. Three grams of calcium sulfate (FCC Grade,
95% purity) were then added slowly and with stirring
to the mixing flask. The mixture was mixed
thoroughly. The mixing flask was chilled in an ice
5   bath and the temperature of the mixture in the mixing
flask was about 8-12°C. The ingredients were
continuously stirred at a rate of about 700 rpm.

Separately, a slurry was made by adding 210.92
ml of RO/DI water to 140.61 g (1.86 moles, after
10 purity adjustment) of calcium hydroxide (FCC Grade,
98% purity) making a final volume of 281.23 ml. The
mole ratio of calcium hydroxide to concentrated
sulfuric acid was about 0.31. The slurry was mixed
well with a high-shear-force mixer until the slurry
15 appeared uniform. The slurry was then chilled to
about 8-12°C in an ice bath and continuous stirred at
about 700 rpm.

The slurry was then slowly added over a period
of 2-3 hours to the mixture, still chilled in an ice
20 bath and being stirred at about 700 rpm.

After the completion of the addition of slurry
to the mixture, the product was filtered through a 5-
micron filter. It was normal to observe a 20% loss
in volume of the mixture due to the retention of the
25 solution by the salt and removal of the salt.

The filtrate was allow to sit for 12 hours, the
clear solution was decanted to discard any
precipitate formed. The resulting product was AGIIS
having an acid normality of 12.

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Example 4

General Method for the Preparation of HAMO

For a 1 L final volume of HAMO, n moles of
organic acid (n is from about 0.01 to about 15) is
5   suspended or dissolved in 2n moles of DI water. To
this mixture is then added monovalent, divalent or
trivalent metal base (hydroxide, oxide, carbonate or
bicarbonate, or combination thereof) as the dry solid
or as a slurry in DI water in the ratio of 1.0
10   equivalent weights of base per equivalent weight of
acid. The addition is accomplished as quickly as
possible. To the resultant mixture is added a
quantity of regenerating acid sufficient to ensure
complete regeneration of the organic acid from its
15   metal salt, but a quantity not greater than 18
moles/L. Preferably, the addition of the
regenerating acid is accomplished as quickly as
possible without permitting the mixture temperature
to rise above 80°C. After the mixing is complete,
20   usually from about 0.5 hour to about 1 hour. the
undissolved solids are removed by filtration through
a 5-micron filter or by centrifugation.

Example 5

Formation of a HAMO from Maleic Acid, Calcium

25   Hydroxide, and Sulfuric Acid

To a mixture of maleic acid (1 kg, 8.61 moles)
and RO-DI water (1 L), solid calcium hydroxide (335
g, 4.52 moles) was added in 50-g portions with
stirring. After the addition of the calcium

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hydroxide was complete, RO-DI water (500 mL) was added. To the resulting mixture, concentrated sulfuric acid (238 mL) was added in 25-mL aliquots at a rate that maintained the reaction temperature below 85°C. The resultant mixture was centrifuged at 15000 rpm for 25 minutes to provide the HAMO as supernatant, pH of 0.5 - 1.0. Analysis showed: Ca, 12,900 ppm; SO_4 159,000 ppm.

Example 6

Formation of a HAMO from Gluconic Acid, Calcium Hydroxide, and Sulfuric Acid

To a stirred mixture of gluconic acid (50%, 1 kg, 2.55 moles) and water (200 mL) was added 97 g (1.3 moles) of solid calcium hydroxide. After the mixing was complete, concentrated sulfuric acid (76 mL) was added as rapidly as possible while keeping the reaction temperature below 85°C. The final mixture was centrifuged at 15,000 rpm for 25 minutes to give the HAMO as supernatant, pH of 1.0. Analysis showed: Ca, 1,210 ppm; SO_4, 11,600 ppm.

Example 7

Formation of a HAMO from Succinic Acid, Calcium Hydroxide, and Phosphoric Acid

Solid calcium hydroxide (320 g, 4.23 moles) was added in 50-g portions to a stirred mixture of succinic acid (1 kg, 8.47 moles) and RO-DI water (1200 mL). Concentrated phosphoric acid (529 mL,

4.75 moles) was added in 50-mL aliquots as rapidly as possible while maintaining the temperature below 85°C. The final product had a pH of 1.5. Analysis showed: Ca, 26,700 ppm; PO$_4$, 250,000 ppm.

5   Example 8
Formation of a HAMO from Acetic Acid, Calcium Carbonate, and Sulfuric Acid

        1. Preparation of Calcium Acetate. One liter (17.48 moles) of acetic acid was added to an eight-
10 liter container, and one liter of water was added. Calcium carbonate powder (874 g, 8.74 mole, 99+%) was added in 100-g portions over 2.5 hours with agitation until the solution was neutral to pH paper. Water was added as needed to maintain fluidity in the
15 mixture during the neutralization.
        2. Formation of the HAMO. Water was added to the calcium acetate formed in step 1 to bring the total volume to 3 gallons. To this solution, 17.48 moles of 95-98% sulfuric acid was added. The mixture
20 was mixed well, and the mixing allowed to proceed without cooling. After the mixing was complete, the mixture was filtered through a 5 micron filter to give the HAMO, pH was 1.15. Analysis showed: Ca, 17,000 ppm; PO$_4$, 158,000 ppm.
25   In smaller scale preparations, it was more convenient to free the HAMO from undissolved solids by centrifugation.

                            Example 9
Formation of a HAMO from Lactic Acid, Calcium
30 Carbonate, and Sulfuric Acid

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1. <u>Preparation of Calcium Lactate</u>. One liter
(11.25 mole) of 85% lactic acid was added to a five-
liter container, and one liter of water was added.
Calcium carbonate powder (874 g, 8.74 mole, 99+%) was
5   added in 100-g portions over 2.5 hours with agitation
until the solution was neutral to pH paper. Water
was added as needed to maintain fluidity in the
mixture during the neutralization.

2. <u>Formation of the HAMO</u>. Water was added to
10   the calcium lactate formed in step 1 to bring the
total volume to 5 gallons. To this solution, 11.25
moles of 95-98% sulfuric acid was added. The mixture
was mixed well, and the mixing was allowed to proceed
without cooling. After the mixing was complete, the
15   mixture was filtered through a 5 micron filter to
give the HAMO, pH of less than 1.0.

In smaller scale preparations, it was more
convenient to free the HAMO from undissolved solids
by centrifugation.

20   **Example 10**

<u>**Formation of a HAMO from Gluconic Acid, Ferrous**</u>
<u>**Hydroxide, and Phosphoric Acid**</u>

Ferrous hydroxide was prepared by the reaction
between 646 grams of ferrous sulfate and 224 grams of
25   sodium hydroxide in RO-DI water to give a final
volume of 2730 mL. The suspension of ferrous
hydroxide obtained in this way was allowed to settle,
the supernatant was removed by decantation, and the
solid was washed three times with water by suspending
30   in a total volume of 2730 mL, allowing the solid to
settle, and decanting the supernatant.

The ferrous hydroxide was suspended in RO-DI
water to give a total volume of 500 mL, and this
mixture was added to a mixture of gluconic acid
(50%, 1 kg, 2.55 moles) and RO-DI water (100 mL).
5   Concentrated phosphoric acid (100 mL) and sucrose (35
g) were added sequentially to this mixture. The
final material did not require filtration or
centrifugation, pH of 1.0. Analysis showed: Fe,
12,800 ppm; Na, 7,450 ppm; PO_4, 90,600 ppm; SO_4,
10 15,800 ppm.

Example 11

Formation of a HAMO from Butyric Acid, Magnesium
Hydroxide, and Phosphoric Acid

To a mixture of butyric acid (500 mL, 5.4 moles)
15 and RO-DI water (500 mL) was added solid magnesium
hydroxide (163.6 g, 2.73 moles) in 25-g portions. To
the resulting mixture was added concentrated
phosphoric acid (180 mL) in 50-mL aliquots. The
final solution had a pH of 1.0. Analysis showed:
20 Mg, 390 ppm; PO_4, 1,560 ppm.

Example 12

Formation of a HAMO from Maleic Acid, Magnesium
Hydroxide, and Phosphoric Acid

Solid magnesium hydroxide (300 g, 97.5%, 5.02
25 moles) was added in 50-g portions to stirred solution
of maleic acid (1 kg, 8.53 moles) in RO-DI water
(1,500 mL). At the end of the adddition, the pH of
the mixture was 5.0. Concentrated phosphoric acid
(338 mL, 85-90%) was added in 25-mL aliquots. No

precipitate was observed during the acidfication
step. The final pH of the HAMO solution was 1.0.
Analysis showed: Mg, 19,500 ppm; PO_4, 287,000 ppm.

Example 13

5 __Formation of a HAMO from Succinic Acid, Magnesium__
__Hydroxide, and AGIIS__

Solid magnesium hydroxide (101 g, 1.16 moles)
was added in two equal portions to a stirred
10 suspension of succinic acid (400 g, 3.39 moles) in
RO-DI water (1 L). After the reaction was complete,
AGIIS (607 mL, 5.58 N) was added in 50-mL aliquots at
a rate that maintained the reaction temperature below
85°C. The solution was centrifuged at 15,000 rpm for
15 about 25 minutes. The pH of the HAMO was 1.0 - 1.5.
Analysis showed: Mg, 24,100 ppm; SO_4, 115,000 ppm.

Example 14

__Formation of a HAMO from Calcium Hydroxide, a Mixture__
__of Acetic, Lactic and Propionic Acids, and Sulfuric__
20 __Acid__

Lactic acid (6 moles), propionic acid (6 moles),
and acetic acid (6 moles) were added to a 5-gallon
container and RO-DI water (1L) was added. Solid
calcium hydroxide (678 g, 9 moles) was added slowly
25 to this mixture with stirring. To this mixture was
added 9 M sulfuric acid (1L, 9 moles H_2SO_4), and water
(3L) as necessary to keep the mixture mobile. The
resultant mixture was filtered through a 5-micron

filter.   The pH of the HAMO was 0.6.   Analysis
showed: Ca, 205 ppm; SO$_4$, 23,900 ppm.

Example 15

5   ## Formation of a HAMO from Calcium Hydroxide, a Mixture
of Formic, Lactic and Propionic Acids, and AGIIS

Lactic acid (6 moles), propionic acid (6 moles),
and formic acid (6 moles) were added to a 5-gallon
container and a saturated solution of calcium sulfate
(1L) was added.   Solid calcium hydroxide (680 g, 9
10   moles) was added to this mixture in 100-g portions
with stirring.   During the addition, the reaction
temperature rose to 85°C.   To this mixture was added
9 M sulfuric acid (950 mL, 8.55 moles H$_2$SO$_4$), AGIIS
(1.2 N, 250 mL, 0.15 moles acid), and water (1L).
15   The resultant mixture was filtered through a 5-micron
filter.   The final HAMO had a pH of 1.0.   Analysis
showed: Ca, 215 ppm; SO$_4$, 17,000 ppm.

Example 16

20   ## Formation of a HAMO from Calcium Propionate and
Sulfuric Acid

RO-DI water (2 L) was placed in an 8-L container
and calcium propionate (5.36 moles) was added.   The
mixture was stirred, and an additional 2.5 L of RO-DI
25   water was added to complete dissolution of the salt.
Concentrated sulfuric acid (300 mL, 5.62 moles) was
added, and the mixture stirred until the reaction was
complete.   The resultant mixture was filtered through

a 5-micron filter.   The pH of the HAMO was 1.5.
Analysis showed Ca, 987 ppm; SO_4, 2,580 ppm.

Example 17

5   **Formation of a HAMO from Calcium Lactate and AGIIS**

To a mixture of 5.60 *N* AGIIS (1 L) and RO-DI
water (1 L) was added solid calcium lactate
pentahydrate (2.79 moles).   The resultant mixture was
allowed to stir without cooling until the mixing was
10   complete.   The final mixture was filtered through a
5-micron filter.   The pH of the HAMO was 2.5 - 3.0.
Analysis showed: Ca, 2,550 ppm; SO_4, 1,090 ppm.

Example 18

Physical Properties of Selected HAMO's

	Description	pH	Ca (ppm) x 10^3	SO_4 (ppm) x 10^3	Mg (ppm) x 10^3	PO_4 (ppm) x 10^3	Other
5 10	Lactic acid HAMO neutralized with $CaCO_3$ and regenerated with sulfuric acid	1.0					Slight yellow tint, Sour/ citrus taste
15 20	Acetic acid HAMO neutralized with $CaCO_3$ and regenerated with sulfuric acid	⟨0.0					
25	Lactic acid HAMO from Ca Lactate and regenerated with 5.6 N AGIIS	2.5-3.0					Slight yellow tint
30 35	Lactic acid HAMO from $CaCO_3$ Lactate and regenerated with 5.6 N AGIIS	⟨0.0	2.55	1.09			Slight yellow tint

Description						
Propionic acid HAMO neutralized with Ca(OH)$_2$ and regenerated with sulfuric acid	1.5	0.917	2.55			
Formic Acid HAMO neutralized with Ca(OH)$_2$ and regenerated with sulfuric acid	1.0-1.5	0.163	3.07			
Lactic acid HAMO neutralized with Ca(OH)$_2$ and regenerated with phosphoric acid		44.6			329	Pickles iron and prohibits rust
Formic acid HAMO neutralized with Ca(OH)$_2$ and regenerated with phosphoric acid	1.0-1.5	22.6			156	
Propionic acid, formic acid, lactic acid HAMO neutralized with Ca(OH)$_2$ and regenerated with sulfuric acid	1.0	0.215	17			

5 10	Propionic acid, lactic acid HAMO neutralized with Ca(OH)$_2$ and regenerated with sulfuric acid	0.6	0.205	23.9			
15 20	Gluconic acid HAMO neutralized with Ca(OH)$_2$ and regenerated with sulfuric acid	1.0	1.21	11.6			Sugar odor
25	Gluconic acid HAMO neutralized with Fe(OH)$_2$ and regenerated with phosphoric acid	1.0	1.28 (Fe)	15.8		90.6	The solution had a faint metallic odor and taste
30 35	Acetic acid HAMO neutralized with CaCO$_3$ and regenerated with sulfuric acid	⟨0.0					
40 45	Acetic acid HAMO from Ca acetate and regenerated with phosphoric acid	2.0-2.5	17			158	

Maleic acid HAMO neutralized with Ca(OH)$_2$ and regenerated with sulfuric acid	0.5-1.0	12.9	15.9			
Maleic acid HAMO neutralized with Ca(OH)$_2$ and regenerated with phosphoric acid	1.0-1.5					
Maleic acid HAMO neutralized with Mg(OH)$_2$ and regenerated with sulfuric acid	0.5		163	34.9		
Maleic acid HAMO neutralized with Mg(OH)$_2$ and regenerated with phosphoric acid	1.0			19.5	287	
Lactic acid, propionic acid, acetic acid HAMO neutralized with Ca(OH)$_2$ and regenerated with 10 N AGIIS	≪0.0					

Butyric acid HAMO neutralized with Ca(OH)$_2$ and regenerated with phosphoric acid		0.589			7.16	
Butyric acid HAMO neutralized with Ca(OH)$_2$ and regenerated with phosphoric acid				0.390	1.56	
Succinic acid HAMO neutralized with Ca(OH)$_2$ and regenerated with phosphoric acid	1.5	26.7			250	
Succinic acid HAMO neutralized with Ca(OH)$_2$ and regenerated with sulfuric acid	0.5-1.0	0.500	31			
Succinic acid HAMO neutralized with Ca(OH)$_2$ and regenerated with 5.58 N AGIIS	1.0-1.5	0.443	23.5			

Succinic acid HAMO neutralized with Mg(OH)$_2$ and regenerated with 5.58 N AGIIS	1.0-1.5		115	24.1		

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Example 19

<u>Formation of a HAMO from Glycine, Calcium Hydroxide and Sulfuric Acid</u>

Glycine (37.55 g, 0.5 moles) was suspended in DI
5   water (100 mL) and solid calcium hydroxide (18.55 g,
0.25 moles) was added to the vigorously stirred
suspension. The mixture was allowed to stir at room
temperature for 30 minutes, and was then diluted to a
volume of 350 mL with DI water. Concentrated
10   sulfuric acid (27 mL, 55.6 g, 0.56 moles) was added
as rapidly as possible without causing the mixture to
rise above 85°C. The final mixture was allowed to
stir for 30 minutes, and was then diluted to a final
volume of 500 mL with DI water, and stirred a further
15   1 hour. The mixture was filtered through a medium-
porosity glass sinter to give the HAMO.

Example 20

<u>Formation of a HAMO from Glutamic Acid, Calcium Hydroxide and Sulfuric Acid</u>

20   Glutamic Acid (58.88 g, 0.4 moles) was suspended
in DI water (100 mL) and solid calcium hydroxide
(27.6 g, 0.4 moles) was added to the vigorously
stirred suspension. The reaction mixture became
noticeably warm. The mixture was allowed to stir at
25   room temperature for 45 minutes, and was then diluted
to a volume of approximately 350 mL with DI water.
Concentrated sulfuric acid (28 mL, 57.5 g, 0.57
moles) was added as rapidly as possible without
causing the mixture to rise above 85°C. The final
30   mixture was allowed to stir for 30 minutes, and was

then diluted to a final volume of 500 mL with DI
water, and stirred a further 1 hour. The mixture was
filtered through a medium-porosity glass sinter to
give the HAMO. Analysis showed: Ca, 646 ppm; SO_4,
5   5,120 ppm.

Example 21
Formation of a HAMO from Glutamic Acid, Basic Copper(II) Carbonate and Phosphoric Acid

10   Glutamic Acid (58.88 g, 0.4 moles) was suspended
in DI water (100 mL) and solid basic copper carbonate
(55.2 g, 0.25 moles of $CuCO_3 \bullet Cu(OH)_2$) was added to the
vigorously stirred suspension. The mixture became
extremely viscous and slow effervescence was
15   observed. The mixture was stirred at ambient
temperature for 24 hours to complete the reaction.
Concentrated phosphoric acid (53.6 g, 86.5%, 0.47
moles) was added to the vigorously stirred mixture in
a single aliquot, and the mixture was stirred for 24
20   hours. Constant stirring was required to prevent the
mixture from setting solid. Filtration of the
mixture through a medium porosity sintered glass
funnel provided the HAMO as a deep blue solution.

Example 22
Formation of a HAMO from Glutamic Acid, Basic Cobalt(II) Carbonate and Phosphoric Acid

          Glutamic Acid (58.3 g, 0.4 moles) was suspended
in DI water (200 mL) and solid basic cobalt carbonate
(81.35 g, 0.16 moles of $2CoCO_3 \bullet 3Co(OH)_2$) was added to
30   the vigorously stirred suspension. The mixture

became viscous and slow effervescence was observed.
The mixture was stirred at ambient temperature for 24
hours to complete the reaction. Concentrated
phosphoric acid (53.6 g, 86.5%, 0.47 moles) was added
5   to the vigorously stirred mixture in a single
aliquot, and the mixture was stirred for 24 hours.
Constant stirring was required to prevent the mixture
from setting solid. Filtration of the mixture
through a medium porosity sintered glass funnel
10   provided the HAMO as a pink solution.

Example 23

General Method for the Formation of an Amino Acid

HAMO Using 1.2 M Sulfuric Acid as Regenerating Acid

A solution of dilute sulfuric acid approximately
15   1.2 M in sulfuric acid was prepared by weighing
111.64 g of concentrated (96-98%) sulfuric acid and
diluting with water to 1000.0 mL.
The amino acid or its hydrochloride salt (0.025-
0.1 mole) was weighed into an Erlenmeyer flask and
20   approximately 10 mole equivalents of water was added.
Solid calcium hydroxide (7.40 g, 0.10 mol) was added
to the flask and the mixture was stirred at room
temperature for 30 minutes to ensure complete
reaction. The dilute sulfuric acid (84.0 mL, 0.10
25   moles H_2SO_4) was then added to the mixture. The
mixture was filtered through a medium-porosity glass
frit to give the HAMO. The total acid content of
the HAMO was determined by titration against standard
tris-(hydroxymethyl)aminomethane ("THAM").

HAMOs Prepared From Amino Acids by This Method

Amino Acid	Moles of Amino Acid	[H₃O⁺] in HAMO*
L-glutamine	0.10	0.133 M[1]
L-phenylalanine	0.05	0.185 M[2]
L-asparagine	0.10	0.070 M[3]
L-histidine•HCl	0.10	0.57 M
L-glutamic acid	0.10	0.124 M[4]
L-aspartic acid	0.10	0.170 M[5]
L-lysine.HCl	0.10	0.56 M[6]
L-leucine	0.10	0.173 M[7]
L-alanine	0.10	0.099 M[8]
L-isoleucine	0.02	0.351 M[9]
L-serine	0.025	0.274 M

*Molarity

1.   Ca, 844 ppm   ;   SO₄, 3,120 ppm.
2.   Ca, 390 ppm   ;   SO₄, 13,900 ppm.
3.   Ca, 625 ppm   ;   SO₄, 3,120 ppm.
4.   Ca, 646 ppm   ;   SO₄, 5,120 ppm.
5.   Ca, 1,290 ppm ;   SO₄, 3,850 ppm.
6.   Ca, 1,910 ppm ;   SO₄, 7,560 ppm.
7.   Ca, 329 ppm   ;   SO₄, 315,000 ppm.
8.   Ca, 1,230 ppm ;   SO₄, 4,480 ppm.
9.   Ca, 749 ppm   ;   SO₄, 314,000 ppm.

HAMOs Prepared With Amino Acids and Metal Bases*

Amino Acid	Metal Base	Regenerating Acid
L-glutamine	$Ca(OH)_2$	H_2SO_4
L-phenylalanine	$Ca(OH)_2$	H_2SO_4
L-asparagine	$Ca(OH)_2$	H_2SO_4
L-histidine•HCl	$Ca(OH)_2$	H_2SO_4
L-glutamic acid	$Ca(OH)_2$	H_2SO_4
L-aspartic acid	$Ca(OH)_2$	H_2SO_4
L-lysine•HCl	$Ca(OH)_2$	H_2SO_4
L-leucine	$Ca(OH)_2$	H_2SO_4
L-alanine	$Ca(OH)_2$	H_2SO_4
L-isoleucine	$Ca(OH)_2$	H_2SO_4
L-serine	$Ca(OH)_2$	H_2SO_4
glycine	$Ca(OH)_2$	H_2SO_4
L-glutamic acid	$CuCO_3•Cu(OH)_2$	H_3PO_4
L-glutamic acid	$2CoCO_3•3Co(OH)_2$	H_3PO_4
L-glutamic acid	$MnCO_3$	H_3PO_4

5

10

15

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*Each of the product has a pH of lower than about 3.

Example 24

Using HAMO to Decontaminate Apples

Each apple in this experiment was immersed in an
E.coli O157:H7 culture containing 8.8 X 10^8/ml for 5
minutes, and then air-dried at room temperature for
about 24 hours. In one group, a volume of 300 ml of
HAMO (prepared from acetic acid using phosphoric acid
as the regenerating acid. The pH of the HAMO was
1.13) was used to decontaminate E.coli O157:H7-
contaminated apples for 1 minute with shaking. In
another group, the control group, each of the
contaminated-apple was treated with 300 ml of
sterilized saline. After treatment, each apple was
homogenized. A comparison of plate-counts between
treated and control group was made. The saline
treated apple had 5.37 X 10^5/g (5.32 X 10^7/apple)
survival of E.coli O157:H7; while the HAMO treated
apple had 4.4 X1 0^1/ml (4.39 X 10^3/apple) survival of
E.coli O157:H7. Each of the treated and untreated
apple weighed about 99 g.

Example 25

Using HAMO to Prolong the Shelf-Life of Sausages

Half a pack of non-preserved sausages was dipped
in HAMO (prepared from propionic acid using AGIIS as
the regenerating acid. The pH of the HAMO was 1.51)
for about 0.5 minute, and then packed into a zip-lock
bag. The bag was then left at room temperature for
72 hours. In parallel, the other half pack of the
sausage was dipped in the same amount of autoclaved
de-ionized water. After 72 hours at room

temperature, the control group of sausage was rotten;
while the HAMO treated group was still fresh. The
HAMO treated sausages had over 9-logs reductions in
total bacterial counts compare with control group
5   (i.e. from 9.55 X 10^9/sausage for the control to an
amount that was undetectable in the treated sausage).

Example 26
"Sanitizing" Chopping Board With HAMO

Two small chopping board were inoculated with
10 5ml of E.coli O157:H7 culture (3.55 X 10^8/ml). The
board were then air-dried overnight. One board was
then soaked for 5 minutes with 10 ml of HAMO
(prepared from acetic acid using phosphoric acid as
the regenerating acid. pH of the HAMO was 1.13).
15 The board was then wiped 3 times with sterile gauze,
each gauze was then soaked in 20 ml of saline
solution in a stomacher bag and the bag was stomached
at high speed for 2 minutes. Then the serial
dilution was performed to determine the bacterial
20 survival.. A parallel control was performed using 10
ml of de-ionized water to treat the chopping board.
The result shows the water treated chopping board had
a survival E.coli O157:H7 level of 3.96 X 10^5/ board,
while the HAMO treated one had no E.coli O157:H7 that
25 could be detected.

Example 27

Prolonging Shelf-Live of Cheese With HAMO

A block of mild cheddar cheese (about 8 oz) was sprayed with a solution of HAMO (prepared from
5   propionic acid and AGIIS, the pH value of the HAMO was 1.51). The treated cheese was then stored in a zip lock bag and kept at 4° C. A control block of mild cheddar cheese was stored under identical conditions. After 13 days, mold growth was observed
10   on the control, whereas the treated cheese remained mold free for another 20 days.

What is claimed is:

1.   An acidic composition having an acidic pH value and an acid normality value, the acidic composition comprising:

5   a monovalent or polyvalent cation;

an organic acid; and

an anion of a strong oxyacid,

wherein the acidic composition is less corrosive to a ferrous metal than is a solution of a

10   mineral acid having the same acidic pH value as that of the acidic composition, and

wherein the acid composition is more biocidal than a mixture of the organic acid and a metal salt of the organic acid which mixture having the same acid

15   normality value as that of the acidic composition.

2.   The acidic composition of claim 1, wherein the monovalent cation comprises an ion of Group IA element.

3.   The acidic composition of claim 1, wherein

20   the polyvalent cation comprises an ion of a Group IIA element, but not beryllium.

4.   The acidic composition of claim 1, wherein the polyvalent cation comprises an ion of a Group IIIA element, but not boron.

25   5.   The acidic composition of claim 1, wherein the polyvalent cation comprises a metal of the first transition series.

6.   The acidic composition of claim 1, wherein

the polyvalent cation comprises an ion of magnesium, calcium, ferrous, copper, or zinc.

7.   The acidic composition of claim 1, wherein the polyvalent cation comprises an ion of lead, bismuth, or tin.

8.   The acidic composition of claim 1, wherein the organic acid comprises a carboxylic acid or an acidic vitamin.

9.   The acidic composition of claim 8, wherein the acidic vitamin comprises vitamin C.

10.   The acidic composition of claim 1, wherein the organic acid comprises a monocarboxylic acid, a dicarboxylic acid, or a tricarboxylic acid.

11.   The acidic composition of claim 1, wherein the organic acid comprises acetic acid, lactic acid, formic acid, or propionic acid.

12.   The acidic composition of claim 1, wherein the organic acid comprises an amino acid.

13.   The acidic composition of claim 12, wherein the organic acid comprises glycine, valine, leucine, phenylalanine, lysine, serine, asparagine, glutamic acid, alanine, arginine, aspartic acid, cysteine, histidine, hydroxylysine, hydroxyproline, isoleucine, methionine, proline, threonine, tryptophan, tyrosine, aminoadipic acid, diaminobutyric, ornithine, pepicolic acid, sarcosine or triiodothyronine.

14. An acidic composition prepared by mixing
ingredients comprising:
        at least one regenerating acid having a first
5   number of equivalents;
        at least one metal base having a second
number of equivalents; and
        at least one organic acid,
        wherein the first number of equivalents of
10   the regenerating acid is greater than that of the
second number of equivalents of the metal base.

15. The acidic composition of claim 14, wherein
the regenerating acid comprises a strong oxyacid of
sulfur, phosphorus, nitrogen, chromium, or iodine.

15   16. The acidic composition of claim 14, wherein
the regenerating acid comprises a strong oxyacid of
molybdenum, tungsten, or selenium.

17. The acidic composition of claim 14, wherein
the regenerating acid comprises sulfuric acid,
20   phosphoric acid, or an acidic solution of sparingly-
soluble Group IIA complexes.

18. The acidic composition of claim 17, wherein
the acidic sparingly-soluble Group IIA complex is
prepared by mixing ingredients comprising a mineral
25   acid and a Group IIA hydroxide, or a Group IIA salt of
a dibasic acid, or a mixture thereof.

19. The acidic composition of claim 18, wherein
the Group IIA hydroxide comprises calcium hydroxide,

the mineral acid comprises sulfuric acid, and the Group
IIA salt of the dibasic acid comprises calcium sulfate.

20. The acidic composition of claim 14, wherein
the metal base comprises a hydroxide, a carbonate, a
5   bicarbonate, or an oxide of a metal.

21. The acidic composition of claim 14, wherein
the metal base comprises a base of a Group IA element.

22. The acidic composition of claim 14, wherein
the metal   base comprises a base of a Group IIA
10 element, but not beryllium.

23. The acidic composition of claim 14, wherein
the metal base comprises a base of a Group IIIA
element, but not boron.

24. The acidic composition of claim 14, wherein
15 the metal base comprises a base of a metal of the first
transition series.

25. The acidic composition of claim 14, wherein
the metal base comprises a base of magnesium, calcium,
ferrous, copper, or zinc.

20   26. The acidic composition of claim 14, wherein
the metal base comprises a base of lead, bismuth, or
tin.

27. The acidic composition of claim 14, wherein
the organic acid comprises a carboxylic acid or an
25 acidic vitamin.

28. The acidic composition of claim 27, wherein the acidic vitamin comprises vitamin C.

29. The acidic composition of claim 14, wherein the organic acid comprises a monocarboxylic acid, a dicarboxylic acid, or a tricarboxylic acid.

30. The acidic composition of claim 14, wherein the organic acid comprises acetic acid, lactic acid, formic acid, or propionic acid.

31. The acidic composition of claim 14, wherein the organic acid comprises an amino acid having an amino group, and wherein the number of equivalents of the regenerating acid is greater than the total number of equivalents of the metal base and the amino group of the amino acid.

32. The acidic composition of claim 31, wherein the organic acid comprises glycine, valine, leucine, phenylalanine, lysine, serine, asparagine, glutamic acid, alanine, arginine, aspartic acid, cysteine, histidine, hydroxylysine, hydroxyproline, isoleucine, methionine, proline, threonine, tryptophan, tyrosine, aminoadipic acid, diaminobutyric, ornithine, pepicolic acid, sarcosine or triiodothyronine.

33. An acidic composition prepared by mixing ingredients comprising:
        at least one regenerating acid having a first number of equivalents; and
        at least one metal salt of an organic acid having a second number of equivalents,

wherein the first number of equivalents of the regenerating acid is greater than the second number of equivalents of the metal salt of the organic acid.

34. The acidic composition of claim 33, wherein the regenerating acid comprises a strong oxyacid of sulfur, phosphorus, nitrogen, chromium, or iodine.

35. The acidic composition of claim 33, wherein the regenerating acid comprises a strong oxyacid of molybdenum, tungsten, or selenium.

36. The acidic composition of claim 33, wherein the regenerating acid comprises sulfuric acid, phosphoric acid, or an acidic solution of sparingly-soluble Group IIA complexes.

37. The acidic composition of claim 36, wherein the acidic sparingly-soluble Group IIA complex is prepared by mixing ingredients comprising a mineral acid and a Group IIA hydroxide, or a Group IIA salt of a dibasic acid, or a mixture thereof. -

38. The acidic composition of claim 36, wherein the Group IIA hydroxide comprises calcium hydroxide, the mineral acid comprises sulfuric acid, and the Group IIA salt of the dibasic acid comprises calcium sulfate.

39. The acidic composition of claim 36, wherein the metal salt of the organic acid comprises a salt of a Group IA element.

40. The acidic composition of claim 36, wherein

the metal salt of the organic acid comprises a salt of
a Group IIA element, but not beryllium.

    41.   The acidic composition of claim 36, wherein
the metal salt of the organic acid comprises a salt of
a Group IIIA element, but not boron.

    42.   The acidic composition of claim 36, wherein
the metal salt of the organic acid comprises a salt of
a metal of the first transition series.

    43.   The acidic composition of claim 36, wherein
the metal salt of the organic acid comprises a salt of
magnesium, calcium, ferrous, copper, or zinc.

    44.   The acidic composition of claim 36, wherein
the metal salt of the organic acid comprises a salt of
lead, bismuth, or tin.

    45.   The acidic composition of claim 36, wherein
the organic acid comprises a carboxylic acid or an
acidic vitamin.

    46.   The acidic composition of claim 36, wherein
the acidic vitamin comprises vitamin C.

    47.   The acidic composition of claim 36, wherein
the organic acid comprises a monocarboxylic acid, a
dicarboxylic acid, or a tricarboxylic acid.

    48.   The acidic composition of claim 36, wherein
the organic acid comprises acetic acid, lactic acid,
formic acid, or propionic acid.

49. The acidic composition of claim 36, wherein the organic acid comprises an amino acid having an amino group, wherein the total number of equivalents of the regenerating acid is greater than the total number

5   of equivalents of the metal salt of the organic acid and the total number of equivalents of amino groups from the amino acid.

50. The acidic composition of claim 49, wherein the organic acid comprises glycine, valine, leucine,

10 phenylalanine, lysine, serine, asparagine, glutamic acid, alanine, arginine, aspartic acid, cysteine, histidine, hydroxylysine, hydroxyproline, isoleucine, methionine, proline, threonine, tryptophan, tyrosine, aminoadipic acid, diaminobutyric, ornithine, pepicolic

15 acid, sarcosine or triiodothyronine.

51. An acidic composition prepared by mixing ingredients comprising:
        at least one regenerating acid, wherein the regenerating acid comprises sulfuric acid, phosphoric

20 acid or an acidic solution of sparingly-soluble Group IIA complexes, and wherein the regenerating acid has a first number of equivalents;
        at least one polyvalent base, wherein the polyvalent base is calcium hydroxide, calcium

25 carbonate, or magnesium hydroxide, and wherein the polyvalent base has a second number of equivalents; and
        at least one organic acid, wherein the organic acid is acetic acid, lactic acid, formic acid or propionic acid, and

30   wherein the first number of equivalents of the regenerating acid is greater than the second number

of equivalents of the polyvalent base.

52. The acidic composition of claim 51, wherein the acidic sparingly-soluble Group IIA complex is prepared by mixing ingredients comprising a mineral acid and a Group IIA hydroxide, or a Group IIA salt of a dibasic acid, or a mixture thereof.

53. The acidic composition of claim 52, wherein the Group IIA hydroxide comprises calcium hydroxide, the mineral acid comprises sulfuric acid, and the Group IIA salt of the dibasic acid comprises calcium sulfate.

54. An acidic composition prepared by mixing ingredients comprising:

at least one regenerating acid, wherein the regenerating acid comprises sulfuric acid, phosphoric acid or an acidic solution of sparingly-soluble Group IIA complexes, and wherein the regenerating acid has a first number of equivalents;

at least one salt of an organic acid, wherein the salt is a calcium or magnesium salt of acetic acid, lactic acid, formic acid or propionic acid, and wherein the salt of the organic acid has a second number of equivalents, and

wherein the first number of equivalents of the regenerating acid is greater than the second number of equivalents of the salt or the organic acid.

55. The acidic composition of claim 54, wherein the acidic sparingly-soluble Group IIA complex is prepared by mixing ingredients comprising a mineral acid and a Group IIA hydroxide, or a Group IIA salt of

a dibasic acid, or a mixture thereof.

56. The acidic composition of claim 55, wherein the Group IIA hydroxide comprises calcium hydroxide, the mineral acid comprises sulfuric acid, and the Group IIA salt of the dibasic acid comprises calcium sulfate.

57. A method of preparing an acidic composition, comprising:

dissolving or suspending an organic acid in water to give a solution or suspension of the organic acid;

adding a metal base to this solution or suspension of the organic acid to give a mixture;

adding to the mixture an amount of regenerating acid sufficient to ensure complete regeneration of the organic acid from its metal salt; and

removing the undissolved solid to give the acidic composition.

58. A method of preparing an acidic composition, comprising:

dissolving or suspending a monovalent, divalent or trivalent metal salt of an organic acid to give a solution or suspension of the salt of the organic acid;

adding to the solution or suspension of the salt of the organic acid an amount of regenerating acid sufficient to ensure complete regeneration of the organic from its metal salt; and

removing the undissolved solid to give the
acidic composition.

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 March 2002 (14.03.2002)

PCT

(10) International Publication Number
WO 02/19846 A3

(51) International Patent Classification[7]: A23L 3/3508, 3/3526, 3/358, A23B 7/10, 4/12

(21) International Application Number: PCT/US01/41954

(22) International Filing Date: 30 August 2001 (30.08.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/655,131   5 September 2000 (05.09.2000)   US

(71) Applicant: MIONIX CORPORATION [US/US]: Suite 130, 1376 Lead Hill Boulevard, Roseville, CA 95661 (US).

(72) Inventors: KEMP, Maurice, Clarence; 4401 Woodthrush Drive, El Dorado Hills, CA 95762 (US). LALUM, Robert, Blaine; 6949 Greenback Lane #B, Citrus Heights, CA 95621 (US). LEWIS, David, E.; 816 Third Avenue, Eau Claire, WI 54703 (US). CARPENTER, Robert, H.; 1303 Pecan Street, Bastrop, TX 78602 (US).

(74) Agent: CHWANG, T., Ling; Jackson Walker. L.L.P.. Suite 600, 2435 N. Central Expressway, Richardson, TX 75080 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— with international search report

(88) Date of publication of the international search report:
20 June 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: HIGHLY ACIDIC COMPOSITION COMPRISING AN ORGANIC ACID IN THE PRESENCE OF METAL CATIONS

(57) Abstract: A highly acidic metalated organic acid composition and its preparation. The acidic composition can be prepared by mixing a monovalent or polyvalent cation and an organic acid in the presence of a strong oxyacid, wherein the resultant acidic composition is less corrosive to a ferrous metal than a solution of a mineral acid having the same acidic pH value as that of the acidic composition, and where in the acid composition is more biocidal than a mixture of the organic acid and metal salt of the organic acid which the mixture has the same acid normality value as that of the acidic composition. The acidic composition can be prepared by mixing at least one regenerating acid, at least one metal base, and at least one organic acid, wherein the amount of the regenerating acid is in excess of the equivalent amount of the metal base.

	International Application No
	PCT/US 01/41954

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7   A23L3/3508   A23L3/3526   A23L3/358   A23B7/10   A23B4/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7   A23B   A23L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and. where practical. search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
13 March 2002	03/04/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040. Tx. 31 651 epo nl. Fax: (+31-70) 340-3016	Guyon, R

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